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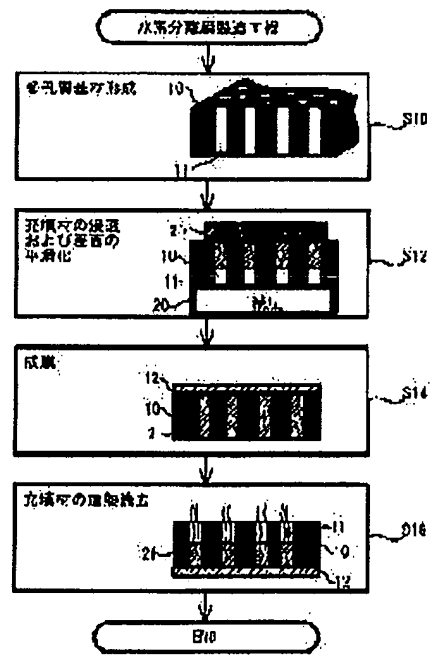
(54) MANUFACTURING METHOD FOR HYDROGEN SEPARATION MEMBRANE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen separation membrane of which thickness can be made thin without generating a pinhole.

SOLUTION: The coating membrane of a hydrogen separation metal is formed on the surface layer of a porous base material to produce the hydrogen separation metal membrane. At this time, the pores of the porous base material are filled with a filler such as paraffin and then membrane formation is carried out. The filler is removed by heating after the film formation. As a result, the sinking and entering of the hydrogen separation metal into the pores of the porous base material can be prevented, thereby making the hydrogen separation metal into a thin membrane while preventing the generation of a pinhole.



CLAIMS

[Claim(s)]

[Claim 1]It is a manufacturing method of hydrogen separation membrane which has hydrogen permselectivity, and is (a). A process of forming a porous base material, (b) A process of covering the surface of this porous base material with a hydrogen separation metal, and forming membranes, and (c) A manufacturing method of hydrogen separation membrane provided with a process of performing processing which controls said hydrogen separation metal permeating into fine pores of said porous base material into this process (b) to said porous base material.

[Claim 2]The manufacturing method comprising according to claim 1:
Said process (c) (c1), A process which fine pores by the side of a film formation surface with which said hydrogen separation metal is covered are made to fill up with a predetermined filler whose melting point is lower than this hydrogen separation metal
(c2) . A process of carrying out heating removal of this filler after said membrane formation

[Claim 3]A manufacturing method which is the manufacturing method according to claim 2, and is a process at which said process (c1) smooths this film formation surface side surface by this restoration.

[Claim 4]A manufacturing method which is the manufacturing method according to claim 2, and is a process to which said process (c2) carries out heating removal of said filler from this film formation surface back side in parallel to said membrane formation.

[Claim 5]A manufacturing method which is the manufacturing method according to claim 1, and is the process of supporting said porous base material under environment where a load in a direction in which said process (c) controls said permeation acts on said hydrogen separation metal.

[Claim 6]A manufacturing method with which it is the manufacturing method according to claim 5, and said porous base material is supported in the state where ambient pressure power by the side of this film formation surface is lower than ambient pressure power on the back side.

[Claim 7]It is a manufacturing method of hydrogen separation membrane which has hydrogen permselectivity, and (a). A process of forming a porous base material, (b) A manufacturing method currently formed as a layer of the minimum aperture in which it has a process of covering the surface of this porous base material with a hydrogen separation metal, and forming membranes, said porous base material has several layers from which an aperture differs in a thickness direction, and the layer of said membrane formation side surface can control permeation of said hydrogen separation metal.

[Claim 8]Are the hydrogen separation membrane which has hydrogen permselectivity, have a porous base material and a hydrogen separation metal layer which covers the surface of this porous base material, and said porous base material, Hydrogen separation membrane currently formed as a layer of the minimum aperture which has several layers from which an aperture differs in a thickness direction, and in which the layer of said membrane formation side surface can control permeation of said hydrogen separation metal.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the hydrogen separation membrane which has hydrogen permselectivity.
[0002]
[Description of the Prior Art]In order to raise the hydrogen purity of the mixed gas of hydrogen and other ingredients, hydrogen separation membrane is used. Hydrogen separation membrane is a film which has the character in which hydrogen moves in the inside of a film, by the hydrogen content pressure deficit on on the side front and back side.
Hydrogen is separable from mixed gas using this character.
As hydrogen separation membrane, the film formed with palladium or a palladium silver alloy and the thing which coated a porous base material like ceramics with these metal are known.
[0003]As art about hydrogen separation membrane using a porous base material, and a manufacturing method for the same, there are art given in JP,1-266833,A, art given in JP,3-288534,A, etc., for example. The former is the art about the manufacturing method of the hydrogen separation membrane which controlled generating of the pinhole, and is art which forms a thin film for metal $LaNi_5$ which has hydrogen separability in the breathability porous substrate which comprised a sintered compact of the stainless steel metal powder, etc. by a sputtering technique. The latter is art which forms membranes by performing electroless deposition which makes Pd-Ag alloy a subject on the surface of a porous base material.
[0004]Since hydrogen permeation speed can be improved by generally making thickness of hydrogen separation membrane thin, the request about thin-film-izing of hydrogen separation membrane is high.
[0005]
[Problem(s) to be Solved by the Invention]However, it was difficult to attain thin film-ization, without producing a pinhole conventionally. Thickness became thick in the portion of fine pores, and the technical problem that a transmission rate fell also occurred.
[0006]Drawing 1 is an explanatory view showing typically the generation factor of the evil in the conventional hydrogen separation membrane. The state where the hydrogen separation membrane 3 was formed in the surface of the porous base material 1 which has the fine pores 2 was shown. The fine pores 2 are actually formed intricately, although typically shown as a vertical hole.
[0007]In an all seems well, the hydrogen separation membrane 3 is formed as a thin film, without producing a pinhole (field A). On the other hand, when thin film-ization is attained, the hydrogen separation membrane 3 may cave in in fine pores, and a pinhole may produce by membranous plasmotomy etc. (field B). When a hydrogen separation metal permeates into fine pores at the time of membrane formation, a thick film part may arise (field C). Generating of a pinhole or a thick film part reduces the reliability of hydrogen separation membrane, and separation performance.
[0008]An object [controlling above-mentioned evil] of this invention is to provide the manufacturing method of the hydrogen separation membrane in which thin-film-izing is possible.
[0009]
[The means for solving a technical problem, and its operation and effect] At this invention, it is (a). The process of forming a porous base material, and (b) The process of covering the surface of this porous base material with a hydrogen separation metal, and forming membranes, (c) The hydrogen separation membrane which has hydrogen permselectivity shall be manufactured through the process of performing processing which controls said hydrogen separation metal permeating into the fine pores of said porous base material into this process (b) to said porous base material. Hydrogen separation membrane as used herein shall mean the whole thing which covered the hydrogen separation metal on the surface of the porous base material. When pointing out the

covering of a hydrogen separation metal itself, the term of a "tunic" is used. Membrane formation means the process of forming a tunic on the surface of a porous base material.
[0010]as a porous base material -- ceramics and a metal cell -- a helmet -- the material of other common knowledge is applicable. As a hydrogen separation metal, although palladium, a palladium alloy, etc. are generally applied, it is not limited to this. The membrane formation can apply various methods, such as screen-stencil, plating, sputtering, chemical vapor deposition (CVD), and physical vapor deposition (PVD).
[0011]According to the manufacturing method of this invention, in a process (b), i.e., stage film formation, permeation of a hydrogen separation metal to inside of fine pores of a porous base material can be controlled. In the conventional hydrogen separation membrane, as for each a pinhole and a thick film part occurring, it had become a factor that a hydrogen separation metal caves in or permeates into fine pores as drawing 1 showed previously. Therefore, generating of a pinhole etc. can be controlled by controlling permeation into fine pores during membrane formation. As a result, the reliability of manufactured hydrogen separation membrane can be improved. It is also possible to attain further thin film-ization of a tunic.
[0012]Various methods are applicable to said process (c). Fine pores by the side of a film formation surface with which said hydrogen separation metal is covered as the 1st mode (c1) shall be equipped with a process (c2) made to fill up with a predetermined filler whose melting point is lower than this hydrogen separation metal, and a process of carrying out heating removal of this filler after said membrane formation.
[0013]By plugging up fine pores with a filler at the time of membrane formation, it can control that a hydrogen separation metal permeates into fine pores. As a filler, paraffin etc. can apply a stable organic system material chemically. You can make it filled up with a filler in fine pores by drawing in heating, for example. A filler can be removed easily, without affecting a tunic and a porous base material by heating, since the melting point is low. May carry out fusion elimination, and it is made to evaporate, and may remove.
[0014]If fine pores are filled up with it to such an extent that the filler can control generating of a pinhole or an extreme thick film part, it is sufficient for it. Therefore, a filler does not need to close thoroughly all the fine pores in a porous base material. Fine pores near the film formation surface should just be plugged up at least. As long as it is a range which can control the above-mentioned evil, some unevenness may remain on the surface of a porous base material.
[0015]However, a desirable thing cannot be overemphasized from a viewpoint in which smoothing this film formation surface side surface controls evil of a pinhole etc. by restoration. Smoothing can be performed by cooling, making a filler fix in fine pores, and shaving a filler of a surplus overflowing from a base material surface, after being filled up with a filler in fine pores by heating suction etc.
[0016]After membrane formation is completed, it is not necessary to start removal of a filler. After membrane formation, what is necessary is just the timing which removal of a filler of a film formation surface completes, and a method of carrying out heating removal of said filler from this film formation surface back side can also be taken in parallel to said membrane formation. If it carries out like this, shortening of a manufacturing process of hydrogen separation membrane can be attained.
[0017]As the 2nd mode of said process (c), it is good also as what supports said porous base material under environment where a load in a direction which controls permeation acts on a hydrogen separation metal at the time of membrane formation. As this load, a pressure, gravity, a centrifugal force, etc. are applicable.
[0018]For example, if ambient pressure power by the side of this film formation surface forms membranes in support of a porous base material in the state lower than ambient pressure power on the back side, permeation into fine pores of a hydrogen separation metal can be controlled according to a pressure differential. If a film formation surface is turned caudad and membranes are formed, permeation can be controlled by operation of gravity. If membranes are formed to a peripheral face, rotating a porous base material, permeation can be controlled by operation of a centrifugal force.
[0019]As a manufacturing method mentioned above and the 2nd method of solving the same technical problem, it is (a) at this invention. A process of forming a porous base material, and (b) When manufacturing hydrogen separation membrane by a process of covering the surface of this porous base material with a hydrogen separation metal, and forming membranes, a porous base material which has the following structure shall be used. It has several layers from which an aperture differs in a thickness direction, and a layer of said membrane formation side surface is a porous base material currently formed as a layer of the minimum aperture which can control permeation of said hydrogen separation metal. In a film formation surface, since the pole diameter is very small, permeation of a hydrogen separation metal can be controlled. A size of the minimum aperture can be set up in an experiment etc. according to a method for film deposition. A penetration of hydrogen is not barred, even if it thickens a porous base material to such an extent that intensity of hydrogen separation membrane is securable by providing a layer of a larger pole diameter than the minimum aperture in parts other than a film formation surface.

[0020]The porous base material of multilayer structure can paste together and manufacture two or more layers manufactured separately. When forming a porous base material with ceramics, integral moulding can also be carried out by calcinating, since a paste of ceramics powder and an organic solvent is centrifuged and density of ceramics powder is biased.
[0021]It is also possible to apply collectively processing which controls permeation of a hydrogen separation metal into fine pores, using a porous base material of multilayer structure.
[0022]
[Embodiment of the Invention]A. The 1st example : drawing 2 is process drawing showing the manufacturing process of the hydrogen separation membrane as the 1st example. The 1st example shows the manufacturing method which controls permeation of the hydrogen separation metal to the fine pores of a porous base material with a filler.
[0023]In this manufacturing process, the porous base material 10 is formed first (Step S10). as the porous base material 10 -- ceramics and a metal cell -- a helmet etc. can be used. What is necessary is just to form the porous base material 10 by the well-known various methods. What is necessary is just to set up suitably the path and void content of the fine pores 11 of the porous base material 10 in consideration of the demand to hydrogen permeation speed, the demand to the intensity of hydrogen separation membrane, etc. Although the fine pores 11 are typically shown by the vertical hole by a diagram, there is no necessity of being a vertical hole.
[0024]Next, the fine pores 11 of the porous base material 10 are made to fill up with the filler 21 (Step S12). As a filler, the melting point is lower than the hydrogen separation metal which forms the porous base material 10 and a tunic, and a chemically stable material can be used, choosing it suitably. Paraffin shall be used in this ex( )le.
[0025]Restoration to the fine pores 11 can be performed in the following procedure. The porous base material 10 is fixed to the decompression jig 20. The decompression jig 20 is a decompression container and the airtightness of the grade which can secure the pressure differential in the surface and rear surface of the porous base material 10 is secured between the decompression jig 20 and the porous base material 10. A filler can be filled up with this state into the inside of the fine pores 11 by decompressing the decompression jig 20, heating the filler 21 a little.
[0026]Here, the filler 21 is the following stage film formation, and it fills up with it in order to control that a hydrogen separation metal infiltrates into the fine pores 11. Therefore, it is sufficient, if it is filled up to such an extent that the fine pores 11 of the surface by the side of the upper surface of drawing 2 are plugged up. It is necessary to not necessarily fill up no fine pores 11 of the porous base material 10.
[0027]In this way, after filling up with the filler 21, the porous base material 10 is cooled and the filler 21 is fixed to the inside of the fine pores 11. Then, the filler 21 of the surplus overflowing into the surface is removed, and the surface is smoothed.
[0028]Next, the tunic 12 of a hydrogen separation metal is formed in the surface of the porous base material 10 with which it filled up with the filler in this way (Step S14). As a hydrogen separation metal, palladium, a palladium allo'' etc. are applicable. The membrane formation can apply various methods, such as screen-stencil, plating, spu(ɔring, chemical vapor deposition (CVD), and physical vapor deposition (PVD). What is necessary is just to set up the conditions at the time of membrane formation suitably according to a method for film deposition. However, it is necessary to take care so that the ambient temperature at the time of membrane formation may not exceed the melting point of the filler 21.
[0029]After membrane formation is completed, heating removal of the filler 21 in fine pores is carried out (Step S16). Heat melting of the filler 21 may be carried out, and it may be removed, and it is made to evaporate and may remove. In the figure, the state of carrying out evaporative removal to top-and-bottom reverse in support of hydrogen separation membrane was illustrated. The filler 21 can be removed without hurting one's tunic 12 by using a film formation surface as the undersurface and carrying out evaporative removal.
[0030]Hydrogen separation membrane can be manufactured by the above process. According to the manufacturing method of this example, the fault resulting from a hydrogen separation metal caving in or permeating into fine pores can be controlled. Therefore, the reliability of the manufactured hydrogen separation membrane can be improved. Thin film-ization of a tunic can also be attained with the improvement in reliability. In particular, also in what is called dry processes, such as sputtering and a physical vapor deposition, very thin reliable hydrogen separation membrane can be manufactured.
[0031]The modification 1 of the A1. the 1st example: In restoration (Step S12) of the filler 21, the processing which smooths the surface of the porous base material 10 may be omitted. Drawing 3 is a sectional view of the hydrogen separation membrane at the time of omitting smoothing. The fine pores of the porous base material 10 are filled up with the filler 21A. Since it has not smoothed, some uneven part exists in the film formation surface side (the field A1, B1). In these fields, the tunic 12A may cave in a little in fine pores, or may turn into a thick

film a little. However, these cave-ins or thick-film-izing do not lead to generating of a pinhole, and the extreme fall of hydrogen permeation speed by existence of the filler 21A. If the filler 21A is filled up with this state, it is clear and it is, it is not necessary to necessarily smooth the surface. A process can be simplified by omitting smoothing. In this case, the surface (surface of the bottom in drawing 2) of the side attached to the decompression jig 20 may be used as a film formation surface.

[0032]The modification 2 of the A2. the 1st example: After membrane formation is completed thoroughly, it is not necessary to start the process of heating removal (Step S16 of drawing 2) of the filler 21. It may carry out in parallel to membrane formation. The filler 21 of a film formation surface surface remains, and should just be clear and be until membrane formation is completed. Shortening of a process can be attained by removing the filler 21 in parallel to membrane formation.

[0033]B. The 2nd example : drawing 4 is process drawing showing the manufacturing process of the hydrogen separation membrane as the 2nd example. The 2nd example shows the manufacturing method which forms membranes under the load conditions which control permeation of the hydrogen separation metal to the fine pores of a porous base material.

[0034]The point which forms the porous base material 10 which covers hydrogen separation membrane first is the same as the 1st example (Step S10). In the 2nd example, membranes are formed under the load conditions shown below, without performing restoration of a filler (Step S13).

[0035]In the 1st mode, a hydrogen separation metal is weighted using a pressure differential. It was typically shown in the upper row in drawing 4. The porous base material 10 is fixed to the jig 20A for application of pressure in this mode. The jig 20A for application of pressure is a pressure vessel. Between the jig 20A for application of pressure, and the porous base material 10, the airtightness of the grade which can secure the pressure differential in the surface and rear surface of the porous base material 10 is secured. Membranes are formed in this state, heightening the pressure in the jig 20A for application of pressure. The method for film deposition can apply various methods like the 1st example. Membranes can be formed according to the pressure differential in the surface and rear surface of the porous base material 10, controlling permeation to the fine pores of a hydrogen separation metal. It is not necessary to necessarily apply the 1st mode to a dry process. By providing a pressure differential in a fluid, it is applicable also like wet processes, such as plating.

[0036]In the 1st mode, if the pressure of the jig 20A for application of pressure is made very high, the membrane formation to a fine-pores part may be checked on the contrary. On the other hand, if a pressure is low, permeation of the hydrogen separation metal into fine pores cannot be controlled. It is necessary to set up the pressurizing condition in the 1st mode suitably according to the pole diameter of a porous base material, a void content, and thickness, taking the influence of both into consideration.

[0037]In the 2nd mode, a hydrogen separation metal is weighted using gravity. It was typically shown in the middle in drawing 4. In this mode, membranes are formed from the undersurface of the porous base material 10. As for a method for film deposition, it is desirable to mainly use a dry process. Membranes can be formed with gravity, controlling permeation of the hydrogen separation metal into fine pores.

[0038]In the 3rd mode, a hydrogen separation metal is weighted using a centrifugal force. It was typically shown in the lower berth of drawing 4. In this mode, the porous base material 10 is supported pivotally pivotable, and membranes are formed to a peripheral face, making it rotate. As for a method for film deposition, it is desirable to mainly use a dry process. Membranes can be formed according to a centrifugal force, controlling permeation of the hydrogen separation metal into fine pores. Its validity is high when the 3rd mode forms hydrogen separation membrane of an axial symmetry form, such as a pipe. In consideration of the membrane formation state to a fine-pores part, it is necessary to set up a centrifugal force, i.e., number of rotations, suitably like the 1st mode in the 3rd mode.

[0039]According to the manufacturing method of the 2nd example, reliability can manufacture the hydrogen separation membrane thin-film-ized highly at processes fewer than the 1st example.

[0040]C. The 3rd example : drawing 5 is process drawing showing the manufacturing process of the hydrogen separation membrane as the 3rd example. In the 3rd example, by using the porous base material of multilayer structure shows the manufacturing method which controls permeation of the hydrogen separation metal to fine pores.

[0041]The 3rd example consists of two processes of formation (Step S11) of a porous base material, and membrane formation (Step S14). In Step S11, the porous base material of multilayer structure with which pole diameters differ is formed. The membrane formation can apply various methods illustrated in the 1st example. A tunic is formed in the layer side with a small pole diameter.

[0042]In this example, the porous base material of a two-layer structure provided with the surface base material 14 which equips the surface of the porous base material 10 provided with the fine pores 11 with a comparatively large aperture with the fine pores 15 was used as a porous base material. The construction material of the

substrates 10 and 14 may be the same, and is good also as a different thing. respectively -- ceramics and a metal cell -- a helmet etc. can be used.

[0043]The substrate of multilayer structure can be formed by manufacturing individually the porous base material 10 and the surface base material 14, and pasting them together. The surface of the porous base material 10 may be coated with the surface base material 14. After centrifuging the mixture of ceramics powder and an organic solvent and biasing the density of ceramics powder, integral moulding may be carried out by fabricating and calcinating. Although the case where pole diameters differed nonsequetially was illustrated with the porous base material 10 and the surface base material 14 by a diagram, you may be the structure of changing continuously. A substrate may be a laminated structure of three or more layers.

[0044]The path of the fine pores 15 of the surface base material 14 makes permeation of a hydrogen separation metal the value of the grade which can fully be controlled. A pole diameter is determined according to a method for film deposition. For example, when using sputtering, it is set as equivalent to a metal droplet, or the diameter not more than it.

[0045]What is necessary is just to set up the thickness of the surface base material 14 to such an extent that permeation of the hydrogen separation metal to the inside of fine pores can fully be controlled at the time of membrane formation. It is desirable to set up thinly in this range. If the surface base material 14 is made extremely thin, a possibility that the surface base material 14 is passed and a hydrogen separation metal permeates into the fine pores of the porous base material 10 will become high. On the other hand, if the surface base material 14 is thickened, the gas permeation nature of hydrogen separation membrane will fall under the influence of the pressure loss in the fine pores 15. According to a method for film deposition, it is necessary to set the thickness of the surface base material 14 suitably in consideration of these influences.

[0046]The pole diameter of the porous base material 10 can be set up arbitrarily. It is set up to such an extent that the fine pores 15 of the surface base material 14 can control permeation of a hydrogen separation metal, this example is sufficient, if it is clear and is, and there are no restrictions in particular in the aperture of the fine pores 15 and the fine pores 11, and the size relation of a void content. However, as for the fine pores 11, it is more desirable than the fine pores 15 to consider it as a major diameter or a high void content. It is because the permeability of the gas in hydrogen separation membrane can be improved.

[0047]According to the manufacturing method of the 3rd example, reliability can manufacture the hydrogen separation membrane thin-film-ized highly at processes fewer than the 1st example.

[0048]As mentioned above, although various examples of this invention were described, it cannot be overemphasized that various composition can be taken in the range which this invention is not limited to these examples and does not deviate from the meaning. For example, about the manufacturing method from the 1st example to the 3rd example, it may combine suitably and you may perform.

[Translation done.]

* NOTICES *

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damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

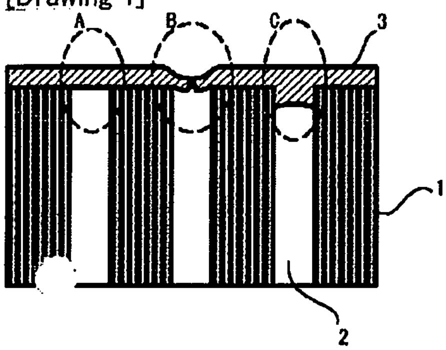
[Brief Description of the Drawings]
[Drawing 1]It is an explanatory view showing typically the generation factor of the evil in the conventional hydrogen separation membrane.
[Drawing 2]It is process drawing showing the manufacturing process of the hydrogen separation membrane as the 1st example.
[Drawing 3]It is a sectional view of the hydrogen separation membrane at the time of omitting smoothing.
[Drawing 4]It is process drawing showing the manufacturing process of the hydrogen separation membrane as the 2nd example.
[Drawing 5]It is process drawing showing the manufacturing process of the hydrogen separation membrane as the 3rd example.
[Description of Notations]
10 -- Porous base material
11 -- Fine pores
12 12A -- Tunic
14 -- Surface base material
15 -- Fine pores
20A -- Jig for application of pressure
20 -- Decompression jig
21 21A -- Filler

[Translation done.]

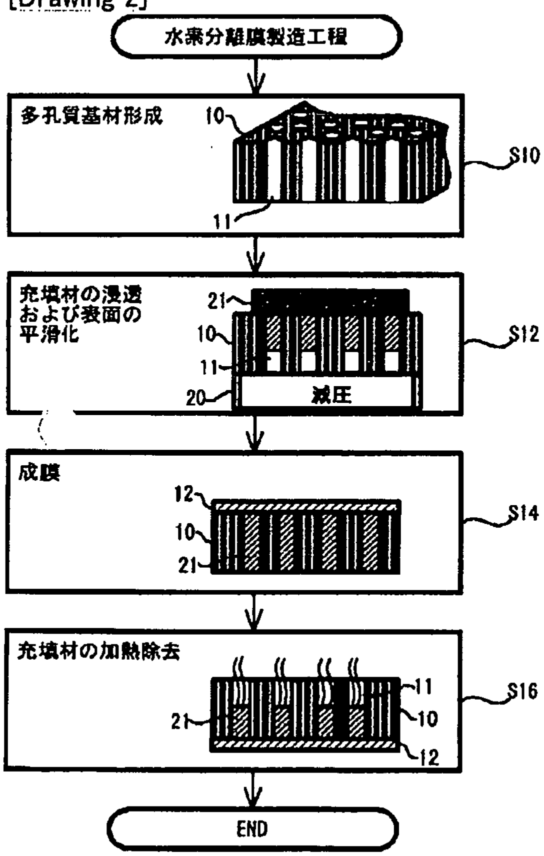
* NOTICES *

DRAWINGS

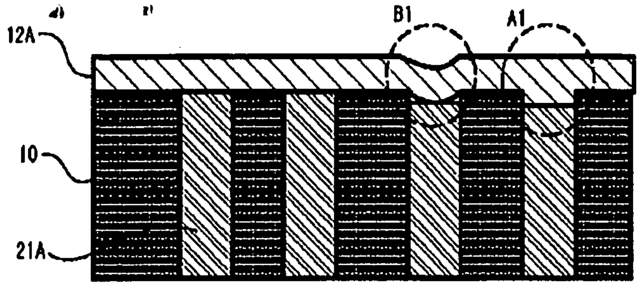
[Drawing 1]



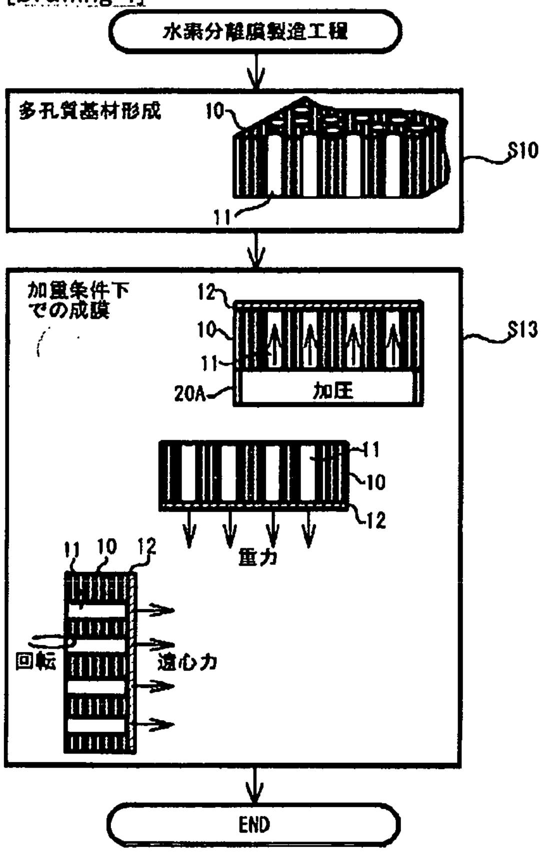
[Drawing 2]



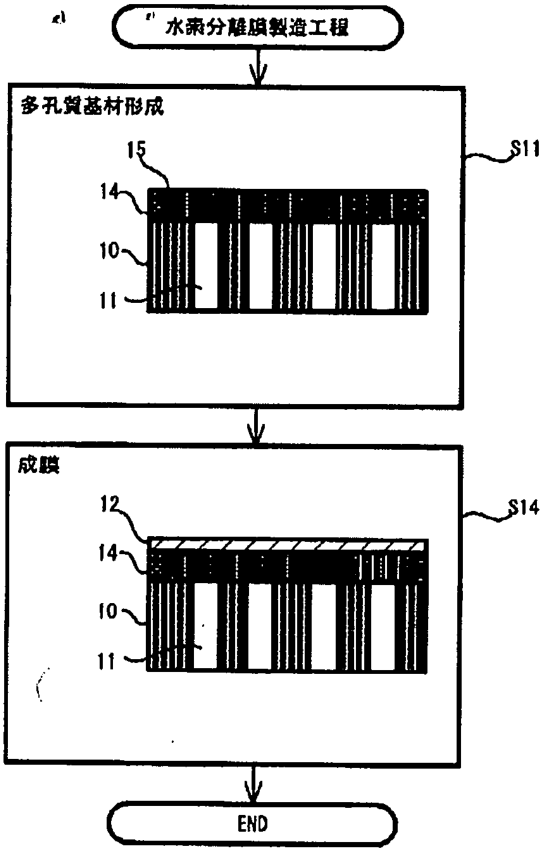
[Drawing 3]



[Drawing 4]



[Dr. .ing 5]



[Translation done.]